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BIOCHEMICAL AND GEOCHEMICAL ORIGINS OF ASH-FORMING INGREDIENTS IN COAL

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ABSTRACT

Coal is a product of geological as well as biological agencies; as such, the ash forming ingredients in the coal have had a complex history. The origins of ash forming ingredients in the coal are traced through the entire cycle of coalification--from the living plant, through the peat stage during burial and compaction, and finally to the weathering stage. Special emphasis is placed upon minor elements, not normally concentrated in the separable minerals, but more likely concentrated by living plants, and by chemical combinations with degradation products of coal flora in the peat stage. Analyses of ash of original peat, and of ash of peat extracts such as humic acids, humins, holocellulose, and alpha cellulose yield significant data relative to the function of degradative products as concentrating agents for heavy transition elements such as Co, Ni, Cu, Zn, Nb, Mo, Sn, Au, Pb, and Bi. Germanium, not detected in any plant ashes, nor in any peat ashes, is found in the ash of humic acid extracts from the same peats. The alkaline and alkaline earth elements are generally lower in the ash of coals and peats than in the ash of plants and the reasons for this are discussed in the light of the life cycle of plants. The low manganese content of plant degradative products and of coal is compared to the high iron content of coal and of plant degradative products.

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INTRODUCTION

Coal is a product of geological as well as biological agencies. All too often the geological aspect of coal is ignored. In general coal technologists and fuel chemists dealing with the whole coal as a substance consider ash-free or mineral matter-free coal as a starting point for processing or for calculation. This is a snare and a delusion unless one always keeps in mind the fact that mineral-matter free or ash-free coal is only a concept and is ideally approached on rare occasions only by careful separation of selected vitrain.

It is entirely improper and quite inaccurate to consider minerals deposited with plant materials in a coal swamp as adventitious matter. Every naturally occurring body of water, from a droplet on the end of a stalactite to an ocean basin, is a suitable environment for mineral deposition. The very existence of coal is dependent upon a rare sequence of geologic events. Each stage contributing to the transformation of living plant material into coal also effects some transfer to what are commonly termed mineral elements.

This paper is concerned with the biochemical as well as the geochemical origins of the ash forming ingredients in coal, and is intended to serve as a guide to the appreciation of the many factors involved in adding and removing elements from an open system throughout the coalification cycle.

Samples and Analysis:--Sixty-nine samples of ash of coal flora, of peat, and of peat extracts have been analyzed spectrographically by the semiquantitative method of Waring and Annell. (1)

Twenty of these samples were from the herbarium of the Smithsonian Institution and an additional plant sample was collected from near the museum grounds in Washington, D.C. These samples were ashed at 600°C in a muffle furnace before being analyzed spectrographically.

Thirteen peat samples were from Rice Lake Bog near Duluth, Minnesota; these samples represented one-foot intervals of a 13-foot core. These samples were ashed at 800°C in a muffle furnace.

Thirty-five samples of ash from seven composite peat samples from Rice Lake Bog, from extracts of humic acids, humins, holocellulose, and alpha cellulose from each of these peat samples were supplied by Professor M. Passer of the University of Minnesota at Duluth. These samples were ashed at 600°C in a muffle furnace.

General Considerations of Ash-Forming Ingredients:--Total mineral matter in coal is taken to be the summation of all elements present which are not constituents of the coal substance--the organic matter itself, which consists of carbon, hydrogen, oxygen, nitrogen, and sulfur.

There is a difference between "minerals" in coal and "mineral matter" in coal. The distinction is an actual one and is not only theoretical. Minerals, in the geological sense, have distinct properties and can, in large part, be physically separated from the organic coal substance, the limitation of separation being physical distribution. Mineral matter in coal includes the minerals in coal, and, in addition, should include those chemically bound elements other than C, H, O, N, and S. Some of these elements, like fluorine and chlorine, are largely removed during combustion or ashing. Other elements like boron and beryllium, make a large contribution to the total ash content because of the oxygen combined with them. In contrast, some carbon may be present as carbonates in minerals; certainly hydrogen and oxygen are present as water or hydroxide in clays; additional oxygen is present in the silica and alumina and other oxides in minerals; nitrogen is rare in minerals in coal. Sulfur as pyrite and as sulfates usually exceeds organic sulfur.

An ultimate analysis for carbon, hydrogen, sulfur, nitrogen, and oxygen accurately represents the composition of the organic matter in coal only when corrections are applied to account for those elements present in the minerals in the coal. Unless a complete mineral analysis is made to determine the composition and the amounts of minerals present in the coal, the corrections can only be made from formulas applied to the ash content of the coal. In the crudest of estimations the percent ash is equated to mineral matter. Parr, among others, recognized this as only a gross approximation and made refinements by applying corrections based on the sulfur content of the coal and sulfate in the ash together with other factors.

King, Maries, and Crossley (2) added factors which were varied depending upon experience with specific British coals. Millot (3) has further modified the King, Maries, and Crossley formula to specifically compensate for mineral matter in carbonaceous shales associated with British coals. These corrections have been given much attention by the fuel scientist and fuel engineer concerned with the inherent fuel value of coal as well as by the research chemist concerned with an accurate analysis of the reactive organic materials.

A thorough investigation of the nature of ash-forming ingredients in coal must consider the fact that the environment of deposition of plant debris--the coal swamp or peat bog--is in essence a medium in which chemical reactions are occurring. Materials are being dissolved and removed from the system; other substances are being added. Some of the materials added are relatively inert while others are highly reactive. The reaction vessel is large--for a small peat bog, the order of acres in area, and for a Carboniferous coal swamp, tens of thousands of square miles. Not all the reactions are proceeding simultaneously, nor will all of the reactions necessarily take place within a given limited area in the coal swamp, but the summation of these reactions should yield a picture which can be logically interpreted.

Thus the possible origins of ash-forming ingredients in coal are:

- A. From elements originally present in coal forming plants and not lost during degradation and coalification.

- B. From elements combined with organic matter during the peat stage.
- C. From elements combined with organic matter during compaction and burial.
- D. From elements combined with organic matter during weathering and oxidation.
- E. From finely divided minerals deposited in the coal swamp.
- F. From minerals formed in the coal during the peat stage and during subsequent geologic history.

The products of these six sources of ash-forming ingredients can be related to terms commonly used by coal technologists. It has previously been suggested by Deul⁽⁴⁾ that the ash-forming ingredients consist of mechanically separable minerals, inseparable minerals, and non-volatile elements organically combined, complexed, or base-exchanged. The use of such terms is better than use of terms like "inherent ash" or "fixed ash", which to many persons implies that the ash is that derived from the original plant substance.

Separable ash and inseparable ash are terms essentially incorrect. One does not separate ash from unburned coal--one only can separate ash-forming ingredients. Anyone who has worked with high-ash coals and attempted to make appropriate corrections in an ultimate analysis will readily understand the inherent inaccuracy in using such a concept.

All ash-forming ingredients are not necessarily minerals--a certain percentage of them are bound with the organic matter as compounds or as complexes. The rest of this paper is a genetic treatment of the origin of ash-forming ingredients in coal.

ELEMENTS IN PLANTS

Before discussing the kinds of mineral matter that are deposited in a coal swamp or in a peat bog, it is necessary to consider the nature of the so-called inorganic elements that were present in the living plants that died, were in part degraded, and later buried under sediments and preserved as coal. The very plants that are now coal cannot be studied but some of the Carboniferous plants and almost all of the Tertiary plants have living relatives. Even though these younger relatives may differ in size and in range of occurrence, they still provide a living link with the past in that their life processes and their nutritive demands are similar to those of their ancestors.

Certain elements are known to be essential to life processes. Although authorities differ in minute details there is a remarkable concurrence of opinion, especially insofar as the plants are concerned. Dean⁽⁵⁾ in a discussion of plant nutrition and soil fertility lists 16 elements considered necessary for the growth of green plants. These are identical to those listed by Miller⁽⁶⁾. Goldschmidt⁽⁷⁾ lists the biophil elements and, though not differentiating between plant and animal life, he includes all 16 elements mentioned by Dean and by Miller. These elements are P, K, Ca, Mg, Fe, Cu, Cl, Mn, Zn, B and Mo, in addition to C, H, O, N, and S. A wide variety of other elements could have been included in this list as growth-promoting or otherwise beneficial elements, but they are not universally beneficial or else they have such a complex metabolic

function that much doubt exists as to the validity of including them as essential elements. However, this doubt in no way prevents consideration of the function of some plants as concentrators of certain elements, irrespective of the nutritional need for the elements so concentrated. Sodium, iodine, and cobalt are known to be present in most green plants, these are essential to animals but have not been proven essential to green plants. Dean (5) recognizes that although silicon and aluminum occur almost universally in plants they perform no recognized function.

Unlike many animals plants have little selectivity of plant nutrients. If plants become rooted in a toxic environment the plant continues to accumulate the toxic element along with the nutrient elements and as a result the organism may perish. Dean (5) states that:

"The rate of nutrient accumulation is not independent of the concentration in the soil solution, and (except for instances of high concentrations) this rate of absorption is proportional to the concentration of a specific ion species. Ion accumulation or absorption thus is regulated by both external and internal factors."

and that:

"In the case of boron (to a lesser degree the other microconstituents) if the soil contains excessive amounts, toxic quantities are absorbed by plants and growth is restricted."

For this investigation, the ash of 21 samples of coal flora have been analyzed spectrographically and examined in an attempt to determine the range of concentrations for the inorganic elements. Sixteen of the twenty-one plants are typical of Carboniferous coal plants and among these 16 specimens eight genera are represented. The Tertiary flora represented five specimens representing five different genera. These 21 samples are the largest collection of such plants known to have been analyzed; and, though there may be some questions as to the selection of materials, the data are by far better than the available analyses of cereal plants and certain crop plants. Use of herbarium samples has considerable merit in that they are plants selected by botanists as representative specimens, and which presumably show no abnormalities. There are many analyses of the ash of wood used for lumber, but there are invariably of low ash heartwood and include none of the bark, stems and leaves.

The semiquantitative spectrographic analyses of ashes of the 21 plants detected 32 elements. Seventeen of these elements were detected in every plant ash 23 were found in more than half, and only nine were detected in less than half of the plant ashes. No plant ash showed fewer than 19 elements; two plant ashes showed 29 of the 32 elements detected. If we add to these elements C, H, O, N, S, and Cl, which are not detectable by the spectrographic technique used, and Zn which was below the limit of detection in all the plant ashes, then 39 elements in all must be present among these plant ashes. A minimum of from 26 to 36 elements is present in each of these plants.

The data from the analyses are tabulated in Figure 1 as a frequency distribution of the elements within the concentration ranges detected. Because of some uncertainty in the exact percentage present the ranges are separated by broken lines, indicating that elements may be present in higher or lower concentrations. Furthermore, elements not detected in certain samples are not assumed to be present in the next lower range, nor are they presumed

to be totally absent, hence, the tapered boundary pointing downward. No doubt lithium is present in all the plant ashes, but the relative insensitivity of this particular analytical method to lithium explains why it was not found in four samples. Cerium, which is much more abundant than lanthanum and neodymium was not detected--probably not because of its lower concentration but rather because its spectral sensitivity is only one-tenth that of lanthanum and neodymium. On the other hand, beryllium is so sensitive to spectral detection, like silver, that its absence in 20 plant ashes is indeed a good indication that it is present in concentrations far below one part per million in the ash.

Variation in the ash contents is large, from as low as 2.9 percent to a high of 59 percent of dry weight--a factor of 20. Within a single genus the ash content does not appear to vary by more than a factor of two. Too few samples were studied to permit more than the grossest generalizations but it does appear that the ash content of various species of a single genus collected from the same locality may show variations as great as specimens of the same genus collected from different localities. The ash content of individual specimens is of no great significance when taken alone, but when compared to that of a group of plant ashes some sensible pattern is discernable.

Median concentrations of the elements estimated by inspection of the data in Figure 1 are compared in Figure 2 to the abundance of elements in the earth's crust (8). Generalizations can be made which, if they have no other purpose, demonstrate the wide range of elemental concentrations exhibited by typical coal flora as shown in Figure 1. In some instances these concentrations may vary by a factor greater than 1000 as for aluminum and titanium, and by a factor of greater than several hundred for manganese, lead, and zirconium, and by factors of from 50 to 100 for many other elements. Even where the median concentration in plant ash is below that of the crustal abundance, the percentage of that element in one or more of the 21 plant ashes exceed the crustal average for the elements titanium, aluminum, and vanadium. For other elements, which are notably enriched in plant ashes, each of the 21 specimens shows concentrations which exceed the crustal abundance; these are Ag, P, Sr, B, Cu, Ba and Pb. These data indicate that a variation by a factor of ten, contrary to the opinion of Horton and Aubrey (9), may well be expected from similar plants collected at the same site.

ELEMENTS IN PEAT

Knowing that elements both essential and nonessential to plant nutrition may be present in the ash of plants in varying concentration the next logical step is to determine the range of elemental concentrations in peat ash of these and other elements not detected in the plant ash.

Spectrographic analyses of peat have been made by Mitchell⁽¹⁰⁾ and by Salmi⁽¹¹⁾ but there is no treatment of analyses in the literature to show a genetic sequence as is presented in this paper.

The analyses of the ash of 13 one-foot samples of the peat are given in Figure 3. The differences in the composition of the peat ash are great, not only from consideration of the percentage of elements present, but from the relatively narrow range of concentration for some of the elements. For ease in comparing the range of concentration of elements in ash of peat to ash of coal flora as shown in Figure 1 the peat ash analyses are presented in the same order in a frequency distribution diagram in Figure 3.

The alkali and alkaline earth elements K, Ca, Mg, Na, Li, Ba and Sr, which are concentrated in plant ashes, are notably depleted in peat ashes. These elements are relatively soluble and are almost immediately lost from plant fluids during the early peat stage.

Manganese and iron, both essential to plant life, show striking differences in geochemical behavior. Compared to their relative concentration in plant ashes, iron is greatly enriched in peat while manganese is depleted. Under the reducing conditions prevalent in a peat swamp manganese is removed while iron is fixed as sulfides.

Zinc, another essential element, present in plant ashes well below the limit of detection by this analytical method, is highly concentrated in peat. Reclaimed peat soils in New York state⁽¹²⁾ have been found to contain concentration of zinc that are toxic for some crops. Probably zinc is lost from plant fluids in the early degradative stages and is fixed by humic acids. Zinc in solution in ground and surface waters would also be fixed in the peat in the same manner.

ELEMENTS PRESENT IN ASHES OF HUMIC ACID EXTRACTS FROM PEAT

The elements Fe, Cu, Mo, Zn, Pb, Cr, Ni, Co, and Sn are more highly concentrated in the humic acid fraction separated from peat than in the peat or any other fraction. The analyses of the ash of humic acid extracts are shown in Figure 4.

Niobium, bismuth, germanium and gold are found in the ash of humic acid fractions. These elements were not detected in plant ashes, in the whole peat ash nor in any other fraction separated from the peat. Tannic acid, a plant extract closely related to and probably included among these humic acids, has long been used to precipitate heavy metals in quantitative analysis. Niobium specifically is subject to precipitation by tannic acid, and, if found at all in an organic environment it is not unexpected that it be in the humic acid fraction.

Of perhaps more interest is the occurrence of germanium in the humic acid fraction. The electronic age has stimulated investigation of coal and flue dusts as possible commercial sources of germanium, but to this time no large readily concentrated sources have been found. It seems most likely that germanium can be concentrated in coal from solution so long as the humic acids have not been condensed or polymerized to the level that they are no longer reactive.

The geological environment of peat deposits is not to be ignored. The data in Figures 3 and 4 are not typical for boron. Boron is highly enriched in plants with respect to the crustal abundance. But the highly mafic rocks underlying these Duluth peats are probably deficient in boron--hence, the plants which formed this particular peat were also boron deficient. Reclaimed peat soils in Minnesota will not support good crop growth unless 50 pounds of borax per acre is added to the soil.

ELEMENTS IN MINERALS FOUND IN COAL

The contribution of detrital minerals to the trace element assemblage in the ash of whole coal is difficult to evaluate. The elements added are most likely the lithophile elements--Si, Al, Fe, Ti, Mg, K, Na, Mn, Ba, Sr and Zr. These elements are also present in large percentages in plant ash and in peat ash. As far as known no unweathered American coals have been fractionated to

separate and concentrate minerals with subsequent analysis of the mineral concentrate and the organic concentrate and then compared with the original coal to determine a mass balance. However, if such a mineral separation from coal were made and the relative concentration of the lithophile elements in the minerals compared to the coal substance, a better appreciation could be had of the importance of detrital minerals to the elemental distribution of ash of whole coal.

Pyrite, iron disulfide, is an important contributor of iron to coal ash. Some weathered lignites with little or no pyrite present, show high concentrations of "organic" iron--probably iron held in combination with reactive humic material.

Sodium chloride, or halite, is now recognized to be a not uncommon mineral in coals, especially in some English and American deposits. Coals, including some in which marine fossils are occasionally found, probably owe some of their sodium chloride content to catastrophic marine invasions, but not all the sodium chloride was necessarily derived from ocean water.

ELEMENTS COMBINED WITH ORGANIC MATTER DURING WEATHERING AND OXIDATION

Coal beds near the surface are subject to oxidation and weathering, especially in fractured strata. Alteration of pyrite is a first indication of this. Near surface coals are rarely free of gypsum formed by interaction of calcium ions in ground water with sulfate ions derived from oxidized sulfide. Oxides of iron will stain coal or may combine with sulfates to form jarosite, a yellow potassium iron sulfate or other sulfates. A simple calculation will show why the ash content rises in weathered coal.

Percolating surface and ground waters may carry elements in solution which will react with the coal substance to form unusual deposits of some trace elements. Recent studies^(13, 14) have shown that uranium and molybdenum are combined with organic matter in low rank coals during weathering and that iron and germanium may be added to coals during this stage as well.

Too few data are at hand for elements other than uranium but it is most likely that chemical reactivity of coal components is an important factor in controlling the amount of an element that can be held by coal. Schopf and Gray⁽¹⁵⁾ have shown that uranium in Dakota lignites is concentrated in those zones which are highest in translucent humic degradation matter--a highly reactive component.

Unless the geological and geochemical history of a coal is well known the elements combined with organic matter during the weathering stage will be difficult to detect because the changes during this stage may well be masked by reactions that proceeded in all previous stages. This fact notwithstanding, the addition of ash-forming elements during weathering and oxidation is always possible in near surface or fractured coals.

SUMMARY

The origins of ash-forming ingredients in coal have been traced from the living plant through to the weathering and oxidation of coal. Elements, rich in plant ashes and leached during degradation are K, Ca, Mg, Na, Li, Ba, and Sr. Elements concentrated in peat and derived in large part from original plants are zinc and boron. Manganese is lost from plants and rarely enriched in coal. The humic acids extracted from peat are enriched in Fe, Cu, Mo, Pb, Cr, Ni, Co, Sn and Zn. The elements Nb, Bi, Ge, and Au were not detected in plant ashes and in peat ashes but are found in the ash of humic acid fractions. Uranium, molybdenum, and perhaps iron and germanium are combined with organic matter in coal during weathering.

Minerals added to coal in the peat stage are the common sedimentary detrital clays. Pyrite is formed in the peat bog and during diagenesis. During weathering, pyrite oxidation forms abundant sulfates with a concomitant increase in ash content.

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The investigation depended upon the cooperation of Dr. J. R. Swallen, Curator of Plants, at the Smithsonian Institution in Washington, D. C., who provided duplicate samples of specimens from the herbarium. Further progress could not have been made without the support and enthusiastic cooperation of Professor Moses Passer, of the Chemistry Department at the University of Minnesota at Duluth, who supplied peat samples, ash of peat and peat extracts and descriptions of the samples.

Special thanks are due to Mona Frank Smith and Helen Worthing of the U. S. Geological Survey for spectrographic analyses of the samples.

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	%	K	Ca	Mg	P	Fe	Mn	B	Cu	Mo	Zn	Si	Al	Na	Ti	Ba	Sr	Pb	Li
PERCENTAGE RANGE OF ELEMENT IN ASH	> 10	17	9	3								11	4						
	5-10	2	6	6								5	3	2					
	1-5	2	6	10	8	2	2					4	5	16	1	1			
	.5-1			2	8	3	3	7				1	1	3	3	8	2	2	
	.1-.5				5	15	4	7	2				6		3	8	17	3	
	.05-.1					1	4	7	15						9	4	2	8	17
	.01-.05						8		4				2		2			1	4
	.005-.01									2					2			7	
	.001-.005									8					1				
	.0005-.001									2	21								
	.0001-.0005									9									

Fig. 1a -- Concentration of elements in ash of 21 coal flora shown as a frequency distribution within percentage ranges.

	%	As	Cr	Zr	V	Ni	Co	Sn	La	Nd	Ga	Y	Yb	Sc	Ag	Be
PERCENTAGE RANGE OF ELEMENT IN ASH	> 10															
	5-10															
	1-5															
	.5-1															
	.1-.5	1														
	.05-.1	20	3	1	3	4		1	2	1						
	.01-.05		6	3		16		4	1	1	2					
	.005-.01		12	7		1	12	7	15	19	7	7		3		
	.001-.005			8	9		9	13			13	12	1	2	8	
	.0005-.001			2	9								7	16	13	1
													13			20

Fig. 1b -- Concentration of elements in ash of 21 coal flora shown as a frequency distribution within percentage ranges.

Element	Crustal Abundance % or ppm	Median Concentration in Plant Ash % or ppm	Enriched or Depleted in plant ash compared to Crustal Abundance	
			<u>E</u>	<u>D</u>
K	2.6%	+10%	E	
Ca	3.6%	+ 5%	-	-
Mg	2.09%	5%	E	
P	0.12%	.5-1%	E	
Fe	5.0%	.1-.5%		D
Mn	0.1%	.1%	-	-
B	1 ppm	1000-5000 ppm	E	
Cu	70 ppm	500-1000 ppm	E	
Mo	1 ppm	10 ppm	E	
Zn	132 ppm	<80 ppm		D
Si	27.7%	10%		D
Al	8.1%	1%		D
Na	2.8%	3%	-	-
Ti	.44%	.05-.1%		D
Ba	250 ppm	5000 ppm	E	
Sr	300 ppm	1000-5000 ppm	E	
Pb	16 ppm	500 ppm	E	
Li	65 ppm	500-1000 ppm	E	
Cr	200 ppm	10-50 ppm		D
Zr	220 ppm	10 ppm		D
V	150 ppm	50 ppm		D
Ni	80 ppm	50-100 ppm	-	-
Co	23 ppm	10 ppm		D
Ag	0.1 ppm	1-5 ppm	E	

Figure 2. Crustal Abundance and Median Concentration of Some Elements Detected in Ash of Coal Flora and Relative Enrichment or Depletion of Elements Detected Compared to Crustal Abundance

%	K	Ca	Mg	P	Fe	Mn	B	Cu	Mo	Zn	Si	Al	Na	Ti	Ba	Sr	Pb	Li
> 10											10	13						
5-10		3			2						3							
1-5	13	8			6													
.5-1		2	4	4	5								6					
.1-5			8	6									7	13				
.05-1			1	3						2					11			
.01-05						2	11	7		8					2	13	1	13
.005-01						11	2	6										
.001-005									2	3							9	
.0005-001									9								3	
.0001-0005									2									

Fig. 3a -- Concentration of elements in ash of 13 peat samples shown as a frequency distribution within percentage ranges.

%	As	Cr	Zr	V	Ni	Co	Sn	La	Nd	Ga	Y	Yb	Sc	Ag	Be
> 10															
5-10															
1-5															
.5-1															
.1-5															
.05-1															
.01-05	13														
.005-01		1	13	13			1			13					
.001-005		12			13	3	2	4			13				
.0005-001						7	3	9	13				13		
.0001-0005					3	7						13			
.00005-00001														1	
.00001-00005														12	13

Fig. 3b -- Concentration of elements in ash of 13 peat samples shown as a frequency distribution within percentage ranges.

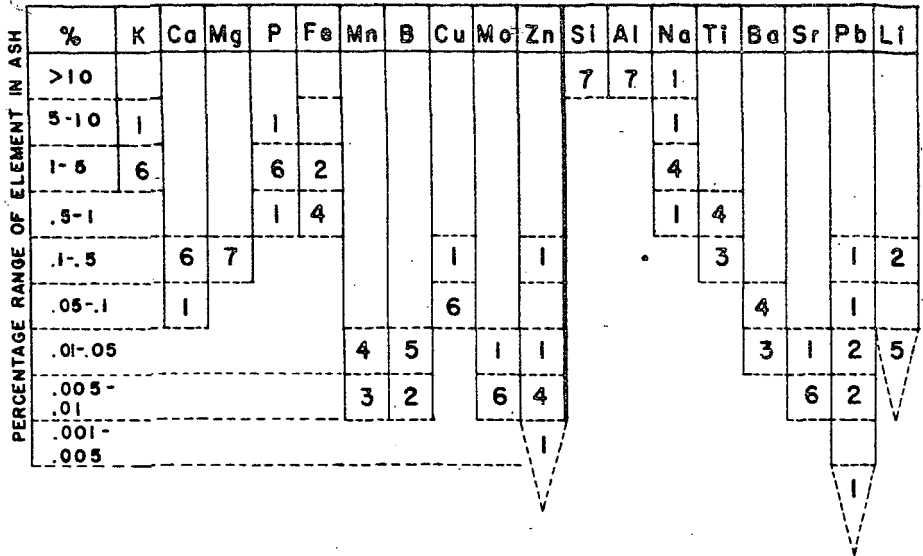


Fig. 4a -- Concentration of elements in ash of humic acid extracts from 7 peat samples shown as a frequency distribution within percentage ranges.

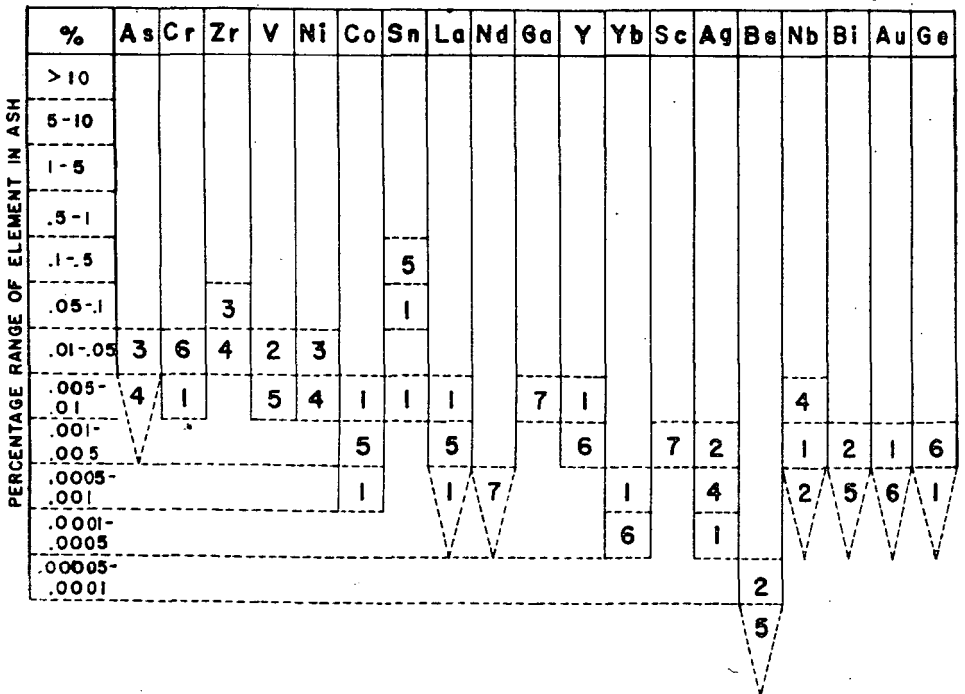


Fig. 4b -- Concentration of elements in ash of humic acid extracts from 7 peat samples shown as a frequency distribution within percentage ranges.